

This is a repository copy of *The Contrasting Character of Early and Late Transition Metal Fluorides as Hydrogen Bond Acceptors*.

White Rose Research Online URL for this paper:

<https://eprints.whiterose.ac.uk/112197/>

Version: Published Version

---

**Article:**

Smith, Dan A., Beweries, Torsten, Blasius, Clemens et al. (8 more authors) (2015) The Contrasting Character of Early and Late Transition Metal Fluorides as Hydrogen Bond Acceptors. *Journal of the American Chemical Society*. pp. 11820-11831. ISSN 1520-5126

<https://doi.org/10.1021/jacs.5b07509>

---

**Reuse**

This article is distributed under the terms of the Creative Commons Attribution (CC BY) licence. This licence allows you to distribute, remix, tweak, and build upon the work, even commercially, as long as you credit the authors for the original work. More information and the full terms of the licence here:

<https://creativecommons.org/licenses/>

**Takedown**

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing [eprints@whiterose.ac.uk](mailto:eprints@whiterose.ac.uk) including the URL of the record and the reason for the withdrawal request.

# The Contrasting Character of Early and Late Transition Metal Fluorides as Hydrogen Bond Acceptors

Dan A. Smith,<sup>†,||</sup> Torsten Beweries,<sup>†,⊥</sup> Clemens Blasius,<sup>†,#</sup> Naseralla Jasim,<sup>†</sup> Ruqia Nazir,<sup>†,▽</sup> Sadia Nazir,<sup>†,○</sup> Craig C. Robertson,<sup>‡</sup> Adrian C. Whitwood,<sup>†</sup> Christopher A. Hunter,<sup>\*,§</sup> Lee Brammer,<sup>\*,‡</sup> and Robin N. Perutz<sup>\*,†</sup>

<sup>†</sup>Department of Chemistry, University of York, Heslington, York, YO10 5DD, U.K.

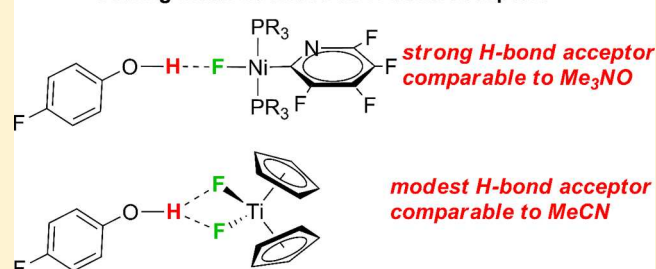
<sup>‡</sup>Department of Chemistry, University of Sheffield, Sheffield, S3 7HF, U.K.

<sup>§</sup>Department of Chemistry, University of Cambridge, Cambridge, CB2 1EW, U.K.

## S Supporting Information

**ABSTRACT:** The association constants and enthalpies for the binding of hydrogen bond donors to group 10 transition metal complexes featuring a single fluoride ligand (*trans*-[Ni(F)(2-C<sub>5</sub>NF<sub>4</sub>)(PR<sub>3</sub>)<sub>2</sub>], R = Et **1a**, Cy **1b**, *trans*-[Pd(F)(4-C<sub>5</sub>NF<sub>4</sub>)(PCy<sub>3</sub>)<sub>2</sub>] **2**, *trans*-[Pt(F){2-C<sub>5</sub>NF<sub>2</sub>H(CF<sub>3</sub>)<sub>2</sub>}(PCy<sub>3</sub>)<sub>2</sub>] **3** and of group 4 difluorides (Cp<sub>2</sub>MF<sub>2</sub>, M = Ti **4a**, Zr **5a**, Hf **6a**; Cp<sup>\*</sup><sub>2</sub>MF<sub>2</sub>, M = Ti **4b**, Zr **5b**, Hf **6b**) are reported. These measurements allow placement of these fluoride ligands on the scales of organic H-bond acceptor strength. The H-bond acceptor capability  $\beta$  (Hunter scale) for the group 10 metal fluorides is far greater (**1a** 12.1, **1b** 9.7, **2** 11.6, **3** 11.0) than that for group 4 metal fluorides (**4a** 5.8, **5a** 4.7, **6a** 4.7, **4b** 6.9, **5b** 5.6, **6b** 5.4), demonstrating that the group 10 fluorides are comparable to the strongest organic H-bond acceptors, such as Me<sub>3</sub>NO, whereas group 4 fluorides fall in the same range as N-bases aniline through pyridine. Additionally, the measurement of the binding enthalpy of 4-fluorophenol to **1a** in carbon tetrachloride ( $-23.5 \pm 0.3$  kJ mol<sup>-1</sup>) interlocks our study with Laurence's scale of H-bond basicity of organic molecules. The much greater polarity of group 10 metal fluorides than that of the group 4 metal fluorides is consistent with the importance of  $p\pi$ - $d\pi$  bonding in the latter. The polarity of the group 10 metal fluorides indicates their potential as building blocks for hydrogen-bonded assemblies. The synthesis of *trans*-[Ni(F){2-C<sub>5</sub>NF<sub>3</sub>(NH<sub>2</sub>)<sub>2</sub>}(PEt<sub>3</sub>)<sub>2</sub>], which exhibits an extended chain structure assembled by hydrogen bonds between the amine and metal-fluoride groups, confirms this hypothesis.

## Scaling metal fluorides as H-bond acceptors



## INTRODUCTION

The studies reported in this paper address the energetics of hydrogen bonding to metal fluoride complexes, placing them on commonly used comparative scales of H-bond acceptor strength. In doing so, we probe the polarity of fluoride complexes down the triads of groups 4 and 10 of the Periodic Table and highlight major differences between them. We also demonstrate that the H-bond ability of group 10 fluoride complexes can be used in supramolecular chain structures.

### Hydrogen Bonding in the Metal–Ligand Domain.

Hydrogen bonding involving metal-bound ligands is crucial to many fields, as is demonstrated in a review including applications in bioinorganic chemistry, photochemistry, organometallic chemistry, and host–guest interactions.<sup>1</sup> Here we are concerned with hydrogen bonding of ligands very close to the metal center, the “ligand domain” as described by Brammer,<sup>2</sup> in which metal and ligand atoms are in strong communication. Critical ligands form hydrogen bonds in numerous metalloproteins, exemplified by Fe(O<sub>2</sub>) ligand in oxymyoglobin, hemoglobin,<sup>3,4</sup> and a nonheme iron dioxygenase.<sup>5</sup> H-Bonding is also significant in heme peroxidase,<sup>6</sup> metal-mediated dioxygen

activation,<sup>7</sup> superoxide dismutases and reductases,<sup>8</sup> and FeCN groups of [FeFe] hydrogenase<sup>9</sup> and is regarded as necessary for proton-coupled electron transfer.<sup>10</sup> H-Bonding is even observed to a metal fluoride unit, MgF<sub>3</sub><sup>-</sup>, in the protein  $\beta$ -phosphoglucomutase.<sup>11</sup> It is increasingly recognized that there are advantages in incorporating hydrogen bonding motifs within the design for metal-based homogeneous catalysts;<sup>12</sup> applications include O<sub>2</sub> activation,<sup>7</sup> hydration and hydro-metalation of alkynes,<sup>13</sup> CO<sub>2</sub> insertion,<sup>14</sup> and reduction of protons and oxidation of H<sub>2</sub>.<sup>15–17</sup> Hydrogen bonds also play an important role in the design of solvent extraction of metal cations. The most effective ligands incorporate “buttressing” by outer-sphere hydrogen bonds to shift the extraction equilibria.<sup>18</sup> In the solid state, hydrogen bonding involving metal complexes has been extensively analyzed from a geometric perspective<sup>19</sup> and has been exploited as a means of supramolecular assembly using a crystal engineering approach.<sup>20</sup> Such hydrogen bonding has enabled the introduction

Received: July 18, 2015

Published: August 24, 2015

of chirality from assembly of achiral components,<sup>21</sup> and has been implicated in the mechanism of solid-state reactions.<sup>22</sup>

An understanding of the energetics of hydrogen bonding to transition metal ligands has been slow to advance. The strongest hydrogen bonds between metal-bound ligands are usually centrosymmetric. Very short intramolecular O...H...O hydrogen bonds are characterized by O...O distances of 2.45–2.50 Å in dioximato complexes.<sup>23</sup> Such complexes play a prominent role as catalysts for water reduction.<sup>16,17</sup> This motif has recently been extended to intramolecular H-bonding between a carboxylic acid and an alkoxide.<sup>12</sup> The absence of systematic thermodynamic data hinders informed design of supramolecular assemblies, especially in systems where multiple sites of differing Lewis basicity compete<sup>24</sup> or where halogen and hydrogen bonding vie for determining the final structure.<sup>25</sup> There are a few exceptions. The engagement of metal hydrides in so-called “dihydrogen bonding” has led to investigations of the energetics of these hydrogen-bonded interactions.<sup>26,27</sup> An exploration of intramolecular hydrogen bond energetics for a wide series of metal-bound ligands has been reported by Crabtree and Eisenstein for the system Ir(H)<sub>2</sub>(Y)(2-C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>)-(PPh<sub>3</sub>)<sub>2</sub>, where Y = F, Cl, Br, I, SCN, and CN.<sup>28,29</sup> These complexes are prearranged to give intramolecular hydrogen bonds between the pendant amine and ligand Y with a measure of the acceptor strength of Y given by the decreasing rotational barrier of the amino group in the order F > Cl > Br > I ~ CN > SCN. An intermolecular example with enthalpy and entropy measurements is provided by the interaction between an OsCl complex and hexafluoroisopropanol.<sup>24</sup>

**Hydrogen Bonding to Metal Fluoride Complexes.** The current interest in organometallic metal fluoride complexes of late transition metals is driven most strongly by metal-mediated fluorination,<sup>30</sup> but carbon–fluorine activation<sup>31</sup> and improved synthetic methods<sup>30–32</sup> are also prominent. The potential of metal fluoride complexes for hydrogen bond formation was recognized by Richmond and co-workers who made measurements on early transition metal fluorides, Cp<sub>2</sub>Ti(F)(X) (X = F, C<sub>6</sub>F<sub>5</sub>) and W(F){κ<sup>3</sup>-C,N,N-(C<sub>6</sub>H<sub>4</sub>)C(H)N(CH<sub>2</sub>)<sub>2</sub>NMe<sub>2</sub>}(CO)<sub>3</sub>.<sup>33–35</sup> The association constants to 4-chlorophenol allowed the Lewis basicity of these compounds to be probed, revealing that W(F){κ<sup>3</sup>-C,N,N-(C<sub>6</sub>H<sub>4</sub>)C(H)N(CH<sub>2</sub>)<sub>2</sub>NMe<sub>2</sub>}(CO)<sub>3</sub> is a stronger H-bond acceptor than Cp<sub>2</sub>TiF<sub>2</sub>. The energetics of the indole...F–[M] hydrogen bonds have been determined for F–[M] = *trans*-[Ni(F)(2-C<sub>5</sub>NEt<sub>4</sub>)(PEt<sub>3</sub>)<sub>2</sub>], **1a**,<sup>36</sup> and tris(2-pyridylthio)methyl zinc fluoride.<sup>37</sup> The ability of metal fluoride complexes to hydrogen bond to HF forming bifluoride complexes is well established from NMR measurements in solution and crystallographic data, but the energetics of the hydrogen bonds are unknown.<sup>38–41</sup> There are also examples of metal fluoride complexes hydrogen-bonded to water that have been established crystallographically and spectroscopically.<sup>42–44</sup> A hydrogen bond between a fluoro-metalate anion and an NH group of a cation is illustrated by [Et<sub>3</sub>NH][Cp\*TaF<sub>5</sub>],<sup>35</sup> while a recent paper describes an iridium fluoride with an intramolecular hydrogen bond to an NH group on an adjacent ligand.<sup>32g</sup> Hydrogen bonds between a gold fluoride and dichloromethane solvent have also been established.<sup>32d</sup>

**Scales for Hydrogen Bond Acceptors.** In contrast to the metal–ligand systems, the energetics of hydrogen bonds involving organic and nonmetal donors and acceptors have been widely studied and scales have been developed by Abraham (β<sub>2</sub><sup>H</sup>),<sup>45,46</sup> Hunter (β),<sup>47</sup> and Laurence (the 4-fluorophenol

affinity scale) to compare the hydrogen bond acceptor strength of different functionalities.

In order to compare interactions of functional groups, a universal scale of hydrogen bond donor and hydrogen bond acceptor strengths was established by Abraham.<sup>49</sup> The intermolecular interactions in dilute solution can be evaluated by eq 1 to obtain the association constant *K* for formation of the hydrogen-bonded complex.

$$\log K = c_1 \alpha_2^H \beta_2^H + c_2 \quad (1)$$

The constants *c*<sub>1</sub> and *c*<sub>2</sub> relate to the solvent medium; α<sub>2</sub><sup>H</sup> and β<sub>2</sub><sup>H</sup> are the dimensionless H-bond donor and acceptor constants of the molecule. The use of these descriptors is well-established in physical organic chemistry, with over 1000 log *K* values determined experimentally for a range of H-bond donors and acceptors, and finds application in the development of linear solvation energy relationships.<sup>50,51</sup> The solvent medium most commonly used for measurements has been carbon tetrachloride, with few other solvents studied in depth. In contrast, Hunter has considered the H-bond acceptor and donor properties of the solvent directly alongside those of the solute, thereby enhancing the transferability of data between solvent media (eq 2).<sup>52</sup> In the Hunter model, α and β remain H-bond donor and acceptor constants but the scales differ from those defined by Abraham (α<sub>2</sub><sup>H</sup> and β<sub>2</sub><sup>H</sup>).

$$\Delta G^0 \text{ (kJ mol}^{-1}\text{)} = -RT \ln K = -(\alpha - \alpha_s)(\beta - \beta_s)E^0 + 6 \quad (2)$$

In eq 2, the free energy of hydrogen bonding interaction, Δ*G*<sup>0</sup> in kJ mol<sup>−1</sup>, is defined in terms of α and β by the consideration of H-bond donor, H-bond acceptor, and solvent interactions, where α and β correspond to the solute molecules and α<sub>s</sub> and β<sub>s</sub> to the solvent; *E*<sup>0</sup> is defined as 1 kJ mol<sup>−1</sup>. This (α − α<sub>s</sub>)(β − β<sub>s</sub>) term is related to *c*<sub>1</sub>α<sub>2</sub><sup>H</sup>β<sub>2</sub><sup>H</sup> in eq 1; the second term in eq 1, *c*<sub>2</sub>, accounts for the energetic penalty of bringing two molecules together in solution to form a noncovalent complex, which is equivalent to the 6 kJ mol<sup>−1</sup> in eq 2 (at 298 K).<sup>49</sup> Rearrangement of eq 2 gives eq 3 that may be solved for β given an experimental determination of *K* and knowledge of α, α<sub>s</sub>, and β<sub>s</sub>.

$$\beta = \beta_s + (RT \ln K + 6)/(\alpha - \alpha_s)E^0 \quad (3)$$

The scales of Abraham and Hunter can be interconverted with eq 4 and 5. To simplify further discussions, we will refer solely to comparisons of β.

$$\alpha = 4.1(\alpha_2^H + 0.33) \quad (4)$$

$$\beta = 10.3(\beta_2^H + 0.06) \quad (5)$$

Importantly, the values of α and β can be estimated accurately by computation of the energetic minima and maxima of the electrostatic potential, *E*<sub>max</sub> and *E*<sub>min</sub>, of the molecule under study and are given in kJ mol<sup>−1</sup> (eqs 6 and 7)<sup>53</sup>

$$\alpha = 2.58 \times 10^{-5}(E_{\max}/E^0)^2 + 7.50 \times 10^{-3}E_{\max}/E^0 \quad (6)$$

$$\beta = c(1.38 \times 10^{-4}(E_{\min}/E^0)^2 - 1.05 \times 10^{-2}E_{\min}/E^0) \quad (7)$$

where *c* is a dimensionless constant that depends on the H-bond acceptor functional group.

Laurence and Graton extended a complementary scale, first proposed by Arnett, that is based on the enthalpic contribution

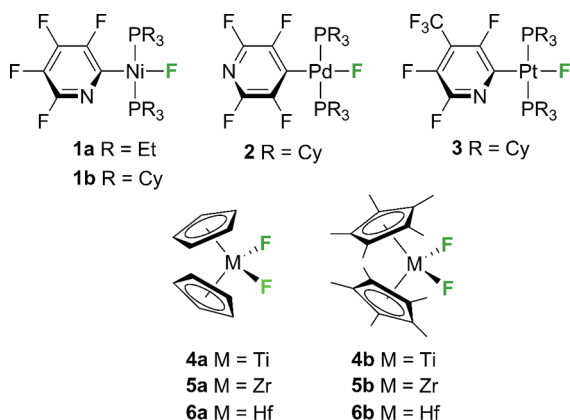
of the binding of Lewis bases with the H-bond donor 4-fluorophenol.<sup>48,54</sup> This donor was chosen for its spectroscopic handles provided by the O–H stretching frequency and the <sup>19</sup>F NMR chemical shift. The solvent of choice for these measurements has been carbon tetrachloride (or tetrachloroethene), selected to minimize the strength of solute–solvent interactions with 4-fluorophenol. The association constants were measured by titration with the concentrations of free and bound 4-fluorophenol determined by monitoring the O–H stretch by IR spectroscopy. Variation of the temperature permitted the enthalpy to be calculated from van't Hoff plots.

**Aims.** The hydrogen-bond acceptor character of transition metal functionalities, such as metal fluorides, hydrides, and cyanides may depend strongly on the nature of the supporting metal and ligands, and their  $\beta$  values remain undetermined to the best of our knowledge. We now report studies involving several H-bond donors of different strength interacting with metal fluoride complexes of groups 10 and 4. As a result, we can place metal fluoride functionalities on the widely used scales of H-bond acceptor character and interlock our measurements with the extensive data for organic moieties. Moreover, this analysis of H-bond strength of metal fluorides provides insight into metal-fluoride bonding, a topic of increasing importance. It also provides design criteria for molecules containing self-complementary groups; we show how we can use these principles to build a H-bonded assembly based on a nickel fluoride complex.

## RESULTS

**Energetics of Binding of H-Bond Donors to Group 10 Metal Fluorides.** Our earlier investigations of *trans*-[Ni(F)(2-C<sub>5</sub>NF<sub>4</sub>)(PEt<sub>3</sub>)<sub>2</sub>] **1a** as both a hydrogen- and halogen-bond acceptor for a narrow selection of organic donor molecules provide an ideal starting point for an extended study (Chart 1).<sup>36,55</sup> Compound **1a** is readily synthesized by

Chart 1. Metal Fluoride Complexes

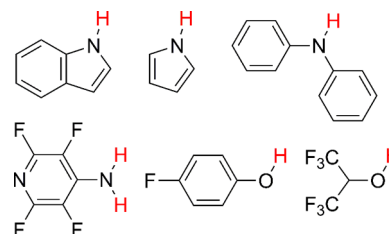


C–F activation of pentafluoropyridine by Ni(COD)<sub>2</sub> with triethylphosphine and fulfills the requirements for this study, namely, possessing a single site of Lewis basicity, high solubility in nonpolar solvents, and an absence of self-association.<sup>56,57</sup> In addition, the <sup>19</sup>F NMR spectroscopic shift of the fluoride is extremely sensitive to its chemical environment with shifts to higher frequency of the order of 20–30 ppm observed at 300 K upon interaction with hydrogen or halogen bond donors. In all cases, only one metal fluoride signal is observed upon introduction of a H-bond donor because of rapid exchange between bound

and unbound forms (see examples of spectra in the Supporting Information). NMR titration methods permit the accurate measurement of binding curves and the determination of their equilibrium constants (eq 8) by fitting the variation in chemical shift with the concentration ratio [RH]/[MF<sub>n</sub>] (RH is the H-bond donor, Chart 2) to an equilibrium expression. The enthalpies and entropies of interaction are derived from van't Hoff plots.



Chart 2. Hydrogen Bond Donors (RH)



**NMR Titration Studies in Toluene.** A series of variable temperature NMR spectroscopic titrations were undertaken with the aim of determining the binding constants and enthalpies of interaction between suitable H-bond donors, RH, and compound **1a** in toluene solution. Hydrogen-bond donors were chosen that possessed high  $\alpha$  values and low  $\beta$  values to disfavor self-association (Table 1, Chart 2). The titration curves for **1a** with diphenylamine are shown in Figure 1. Other curves and sample spectra are provided in the Supporting Information.

The association constants at 300 K of **1a** range from 15.2 ± 0.1 M<sup>−1</sup> for diphenylamine to 15000 ± 1100 M<sup>−1</sup> for the strongest H-bond donor, hexafluoroisopropanol (Table 1).<sup>58</sup> To obtain binding curves amenable to accurate determination of equilibrium constants, the concentration of metal fluoride was chosen according to the expected magnitude of the association constant, with a larger  $K$  requiring a lower concentration. This reciprocal relationship between  $K$  and concentration limited our choice of the strongest H-bond donor to hexafluoroisopropanol, which was measured at [1a] = 5 × 10<sup>−4</sup> M. Measurements for H-bond donors stronger than hexafluoroisopropanol would require even further dilution and would be unsuitable for our extended NMR spectroscopic titrations.

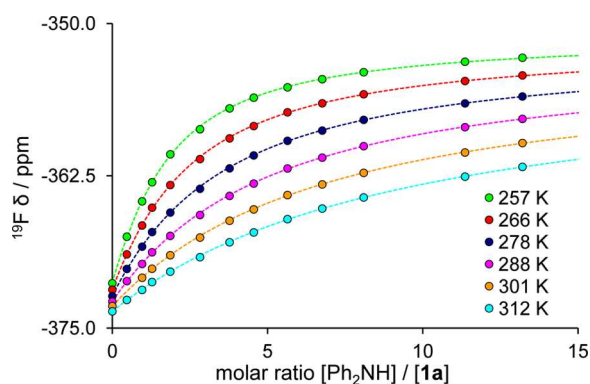
The titration data for **1a** with H-bond donors (Table 1) reveal a good correlation between the equilibrium constant at 300 K and the  $\alpha$  value of the organic donor; i.e., the stronger the donor, the stronger the association. Additionally, a correlation is found between  $\alpha$  and  $-\Delta H^0$  with both decreasing in the order hexafluoroisopropanol (HFIP) > 4-fluorophenol > indole > pyrrole, albeit with a weak alignment of magnitudes. However, diphenylamine is an exception and gave an enthalpy  $\Delta H^0$  comparable to that of indole despite the significantly lower  $\alpha$  value (diphenylamine  $\alpha$  = 2.6, indole  $\alpha$  = 3.2). The higher than expected enthalpy of diphenylamine is accompanied by an increased entropy relative to the other organic H-bond donors measured, resulting in the lowest  $K_{300}$  value of the series. The diphenylamine data reveal the benefits of measuring the full temperature dependence so that enthalpy and entropy can be determined in addition to  $K_{300}$ . The fitting routine for each titration curve models the chemical shift of the adduct in addition to the association constant. For the H-bond donors in Table 1, the differences between the chemical shift of free



Table 1. Thermodynamic Parameters for **1a** *trans*-[Ni(F)(2-C<sub>5</sub>FN<sub>4</sub>)(PEt<sub>3</sub>)<sub>2</sub>]<sup>a,b</sup>

H-bond donor, RH			<b>1a</b>			
	$\alpha$	$\beta$	$K_{300}$ (M <sup>-1</sup> )	$\Delta H^0$ (kJ mol <sup>-1</sup> )	$\Delta S^0$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$\Delta\delta_{300K}^{fit}$
Ph <sub>2</sub> NH	2.6 <sup>f</sup>	1.8 <sup>f</sup>	15.2 ± 0.1	-23.0 ± 0.5	-54 ± 2	20.1
pyrrole	3.0 <sup>d</sup>	4.1 <sup>d</sup>	29.3 ± 0.3	-17.4 ± 0.5	-30 ± 2	20.1
indole <sup>c</sup>	3.2 <sup>c</sup>	3.1 <sup>d</sup>	57.9 ± 0.3	-23.4 ± 0.2	-44.5 ± 0.8	21.7
4-aminotetra-fluoropyridine	3.4 <sup>f</sup>	3.2 <sup>f</sup>	37.9 ± 0.7			21.7
4-fluorophenol	3.9 <sup>d</sup>	2.8 <sup>d</sup>	2800 ± 100	-37 ± 3	-56 ± 11	29.0
HFIP	4.5 <sup>d</sup>	0.9 <sup>d</sup>	15000 ± 1100	-41 ± 3	-56 ± 9	20.8
4-fluorophenol in CCl <sub>4</sub>	3.9 <sup>d</sup>	2.8 <sup>d</sup>	4150 ± 100	-23.5 ± 0.3	-9 ± 1	23.7

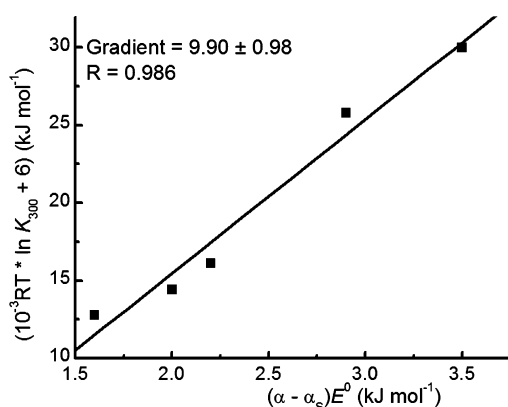
<sup>a</sup>Errors at the 95% confidence level of the fitting routines. <sup>b</sup>Toluene solvent except for the final row where the solvent is CCl<sub>4</sub>. <sup>c</sup>Thermodynamic data taken from ref 36. <sup>d</sup>Taken from ref 53. <sup>e</sup>Determined from ref 46 via eq 4. <sup>f</sup>Determined by DFT from the maxima and minima in the calculated molecular electrostatic potential with a positive point charge in a vacuum as the probe, following eqs 6 and 7; see the Supporting Information for details. See ref 53.



**Figure 1.** Titration curves at different temperatures for diphenylamine and **1a** in toluene, showing  $\delta(^{19}\text{F})$  vs  $[\text{Ph}_2\text{NH}]/[\text{1a}]$ .  $[\text{1a}] = 11$  mM. Circles, experimental points; dashed lines, best fit to a 1:1 binding isotherm.

nickel fluoride and that of the adduct formed,  $\Delta\delta_{300K}^{fit}$ , lie within the range 20–30 ppm, with 4-fluorophenol exhibiting the largest shift.

The association constants  $K_{300}$  and the resulting  $\Delta G^0$  values for a wide range of H-bond donors allow us to assess the H-bond acceptor character of **1a** and quantify its value of  $\beta$ . A plot of  $(RT \ln K_{300} + 6)$  kJ mol<sup>-1</sup> against  $(\alpha - \alpha_s)E^0$  (Figure 2)



**Figure 2.** Determination of  $\beta$  for **1a** from the plot of  $(RT \ln K_{300} + 6)$  versus  $(\alpha - \alpha_s)E^0$  with the gradient equal to  $(\beta - \beta_s)$ .

for the titration data gives a gradient of  $(\beta - \beta_s) = 9.90 \pm 0.98$  (we use  $\alpha_s = 1.0$  and  $\beta_s = 2.2$  for benzene in the absence of values for toluene).<sup>52</sup> Hence, the value of  $\beta$  obtained for **1a** is

$12.1 \pm 1.0$ . Evidently, **1a** is a substantially better H-bond acceptor than either NEt<sub>3</sub> or pyridine, which have  $\beta$  values of 7.5 and 7.2, respectively.<sup>53</sup> The  $\beta$  value of **1a** also exceeds that for trimethylphosphine oxide,  $\beta$  10.7, and is comparable to the value for trimethylamine-*N*-oxide (11.6, calculated for this paper as in ref 53).

Recently, we reported the energetics of halogen bonding to metal fluorides of group 10 metals and demonstrated the tendency of the heavier congeners to be stronger halogen bond acceptors.<sup>55</sup> Direct analogues to **1a** for Pd and Pt are chemically inaccessible, and therefore, the series chosen for this study was **1b**, **2**, and **3** (Chart 1). We showed previously that fluoride Lewis basicity is negligibly affected by changing the *trans* aryl substituent but strongly affected by a change of the phosphine ligands. Complexes **1b**, **2**, and **3**, which each have PCy<sub>3</sub> ligands, can therefore be viewed as a valid series to compare Ni, Pd, and Pt. Titration of each against 4-fluorophenol reveals **2** to exhibit the largest association constant ( $K = 5200 \pm 500$  M<sup>-1</sup>), and **2** is therefore the strongest H-bond acceptor of our study with  $\beta$  of 12.5 (Table 2). The trend in both  $\beta$  and  $-\Delta H^0$  for binding to 4-fluorophenol is described by **2** > **3** > **1b** and is in agreement with the association constants and enthalpies previously determined for halogen bonding to C<sub>6</sub>F<sub>5</sub>I.<sup>55</sup> A comparison of **1a** and **1b** reveals that the change of phosphine from PEt<sub>3</sub> to PCy<sub>3</sub> reduces both  $K_{300}$  ( $2800 \pm 100$  to  $560 \pm 10$  M<sup>-1</sup>) and  $-\Delta H^0$  ( $37 \pm 3$  to  $32 \pm 2$  kJ mol<sup>-1</sup>) for binding to 4-fluorophenol. This decrease is contrary to that expected in terms of electronic effects, since PCy<sub>3</sub> is more electron-donating than PEt<sub>3</sub>.<sup>59</sup> In the reported measurements of halogen bonding from C<sub>6</sub>F<sub>5</sub>I, compound **1a** was a stronger acceptor than **1b** in terms of  $K_{300}$ ,  $3.41 \pm 0.09$  versus  $2.49 \pm 0.16$  M<sup>-1</sup>, but not  $-\Delta H^0$ ,  $16 \pm 1$  and  $18.6 \pm 4$  kJ mol<sup>-1</sup>, respectively. Therefore, a decreased basicity is apparent for **1b** relative to **1a** in the context of our H-bond measurements and indicates a greater steric hindrance of binding to the fluoride exerted by the bulkier cyclohexyl groups. This observation correlates well with the anticipated shorter interaction distance of a hydrogen bond compared to a halogen bond (sum of van der Waals radii; F...H 2.67 Å, F...I 3.45 Å),<sup>60</sup> meaning that the H-bond would suffer to a greater extent from steric hindrance.

**NMR Titration Studies in Carbon Tetrachloride.** The 4-fluorophenol scale of Lewis basicity has been developed by Laurence and co-workers for a range of organic functionalities.<sup>48,51</sup> Titration of **1a** against 4-fluorophenol in carbon tetrachloride gave association constants of  $4150 \pm 100$  M<sup>-1</sup> and an enthalpy of  $-23.5 \pm 0.3$  kJ mol<sup>-1</sup> (Table 1). The association

**Table 2.** Thermodynamic Parameters and  $\beta$  Values for H-Bonding of Group 10 Metal Fluorides with 4-Fluorophenol in Toluene<sup>a–c</sup>

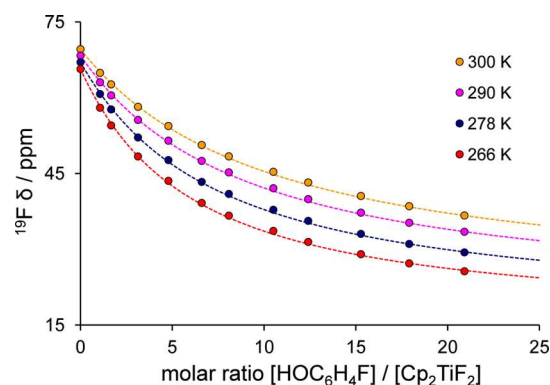
	4-fluorophenol				$\beta$
	$K_{300}$ (M <sup>−1</sup> )	$\Delta H^0$ (kJ mol <sup>−1</sup> )	$\Delta S^0$ (J mol <sup>−1</sup> K <sup>−1</sup> )	$\Delta \delta_{300K}^{fit}$	
<b>1a</b> <i>trans</i> -[Ni(F)(2-C <sub>5</sub> NF <sub>4</sub> )(PEt <sub>3</sub> ) <sub>2</sub> ]	2800 ± 100	−37 ± 3	−56 ± 11	29.0	12.1 ± 1.0 <sup>b</sup>
<b>1b</b> <i>trans</i> -[Ni(F)(2-C <sub>5</sub> NF <sub>4</sub> )(PCy <sub>3</sub> ) <sub>2</sub> ]	560 ± 10	−32 ± 2	−54 ± 6	35.8	9.7
<b>2</b> <i>trans</i> -[Pd(F)(4-C <sub>5</sub> NF <sub>4</sub> )(PCy <sub>3</sub> ) <sub>2</sub> ]	5200 ± 500	−52 ± 1	−101 ± 4	21.7	11.6
<b>3</b> <i>trans</i> -[Pt(F){2-C <sub>5</sub> NF <sub>2</sub> H(CF <sub>3</sub> )}(PCy <sub>3</sub> ) <sub>2</sub> ]	2460 ± 20	−44 ± 1	−83 ± 3	17.8	11.0

<sup>a</sup>Errors at the 95% confidence level of the fitting routines. No error bars are given for values of  $\beta$  calculated for a single H-bond donor. <sup>b</sup>Calculated from the titrations of monohydrogen bond donors in Table 1. The value of  $\beta$  calculated from the 4-fluorophenol data alone is 11.1. <sup>c</sup>Solvent values used:  $\alpha_S = 1.0$ ,  $\beta_S = 2.2$ .

constant and the value of  $-\Delta H^0$  are greater than the analogous toluene measurement, but the value of  $-\Delta S^0$  is considerably smaller. Inspection of the reported enthalpy data for organic molecules reveals THF ( $\Delta H^0$  −23.7 kJ mol<sup>−1</sup>,  $\Delta S^0$  −35.5 J mol<sup>−1</sup> K<sup>−1</sup>) to be a reasonably close comparison for **1a**, whereas the value of  $-\Delta H^0$  is slightly greater for DMF ( $\Delta H^0$  −24.8 kJ mol<sup>−1</sup>,  $\Delta S^0$  −24.1 J mol<sup>−1</sup> K<sup>−1</sup>).<sup>48</sup> The enthalpy of the metal fluoride **1a** binding to 4-fluorophenol is of far greater magnitude than those determined for fluoroalkanes in carbon tetrachloride (1-fluoropentane  $\Delta H^0$  −10.5 kJ mol<sup>−1</sup>). However, the values of  $-\Delta S^0$  for THF and DMF are far greater than those for **1a**.

**Energetics of Binding of H-Bond Donors to Group 4 Metal Fluorides.** We were interested in extending our study beyond the group 10 fluorides to earlier transition metal fluorides. Structural analogues to **1a** are not chemically accessible for the early metals, and thus, a new set of well-defined fluorides free of competing sites of Lewis basicity was needed. The bis- $\eta^5$ -cyclopentadienyl motif, Cp<sub>2</sub>MF<sub>2</sub> (Cp =  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>), fulfilled this requirement and presented a structure that can be systematically varied in terms of both central metal and substitution of the cyclopentadienyl ligands. This choice of structure favored the study of group 4 for which the desired fluorides, Cp<sub>2</sub>MF<sub>2</sub>, are well-known,<sup>61–63</sup> whereas analogues for groups 5 and 6 periodic series have yet to be reported.<sup>35,64,65</sup>

<sup>19</sup>F NMR Studies of Binding. The <sup>19</sup>F NMR resonances for d<sup>0</sup> Cp<sub>2</sub>MF<sub>2</sub> compounds are located at positive or near-positive chemical shifts (Cp<sub>2</sub>TiF<sub>2</sub>  $\delta$  65.1 in CDCl<sub>3</sub>) and contrast with those of group 10 that lie at far higher field (**1a**  $\delta$  −371.4 in C<sub>6</sub>D<sub>6</sub>). Addition of HFIP or 4-fluorophenol to Cp<sub>2</sub>TiF<sub>2</sub> resulted in a movement of the fluoride chemical shift to higher field ( $\Delta\delta < 0$ , Figure 3), whereas for the group 10 fluorides a shift to lower field was observed.<sup>58</sup> NMR titrations of Cp<sub>2</sub>TiF<sub>2</sub> **4a**, Cp<sub>2</sub>ZrF<sub>2</sub> **5a**, and Cp<sub>2</sub>HfF<sub>2</sub> **6a** with the H-bond donor HFIP and with 4-fluorophenol were undertaken in dichloromethane due to their exceptionally poor solubility in toluene and produced binding curves suitable for fitting (Figure 3, Table 3). As would perhaps be expected from their similar chemistries, **5a** and **6a** give similar association constants with HFIP of  $3.8 \pm 0.1$  and  $3.1 \pm 0.1$  M<sup>−1</sup>, whereas titration of **4a** gave a larger association constant of  $9.6 \pm 0.2$  M<sup>−1</sup>. More striking is the comparison to the association constant of **1a** with HFIP that has a  $K_{300}$  value of  $15000 \pm 1100$  M<sup>−1</sup>, a difference of 3 orders of magnitude (which cannot be accounted for by the change in solvent medium from toluene to dichloromethane that would be expected to result in an approximate change of a factor of 2;<sup>52</sup> see the Discussion). A similar difference is observed for titrations of 4-fluorophenol with **4a–6a**, where  $K_{300}$  is much lower than that for **1a**, **2**, and **3** (e.g., **4a**  $4.6 \pm 0.1$ , **1a**  $2800 \pm 100$  M<sup>−1</sup>). The periodic trend observed for the association



**Figure 3.** Titration curves at different temperatures for **4a** and 4-fluorophenol in dichloromethane, showing  $\delta(^{19}\text{F})$  of the metal fluoride vs  $[\text{HOC}_6\text{H}_4\text{F}]/[\text{4a}]$ .  $[\text{4a}] = 23 \text{ mmol dm}^{-3}$ . Circles, experimental points; dashed lines, best fit to a 1:1 binding isotherm.

constants with HFIP, namely, **4a** > **5a** ~ **6a**, is mirrored for titrations of 4-fluorophenol. Examination of the energetics for 4-fluorophenol shows a narrow variation of  $-\Delta H^0$  within the range 11–14 kJ mol<sup>−1</sup> with no clear trend. Instead, the changes in  $\Delta S^0$  account for the differing  $K_{300}$  values with the binding of **4a** to 4-fluorophenol possessing an entropic contribution near half of that measured for binding of **5a** and **6a** to the same donor.

The difference in  $K_{300}$  between **4a–6a** and **1a**, **2**, and **3** is dramatic, but given the variation of solvent, we sought to compare identical solvent media and therefore turned to the pentamethylcyclopentadienyl metal fluorides, Cp<sup>\*</sup><sub>2</sub>MF<sub>2</sub> (Cp<sup>\*</sup> =  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>), for greater solubility in hydrocarbon solutions. The complexes Cp<sup>\*</sup><sub>2</sub>TiF<sub>2</sub> **4b**, Cp<sup>\*</sup><sub>2</sub>ZrF<sub>2</sub> **5b**, and Cp<sup>\*</sup><sub>2</sub>HfF<sub>2</sub> **6b** were readily synthesized by modifications of known procedures, and workable concentrations in toluene could easily be achieved even at low temperatures (e.g., 250 K). <sup>19</sup>F NMR titrations of **4b–6b** with 4-fluorophenol at 300 K showed, as with the series **4a–6a**, that the titanium complex is the strongest H-bond acceptor by a substantial margin (Table 3).

Our data for **4a** can be compared with the initial work of Richmond and co-workers where  $K_{290}$  for the binding of 4-chlorophenol with **4a** and Cp<sub>2</sub>Ti(F)(C<sub>6</sub>F<sub>5</sub>) were found to be 5.6 and 3.9 M<sup>−1</sup> (CDCl<sub>3</sub>), respectively.<sup>33</sup> The values reported by Richmond are of a similar magnitude to those recorded for **4a**, but a more detailed analysis is precluded by the slight differences in the two experimental methods in terms of phenol, solvent, and temperature. The values of  $\beta$  for **5a** and **6a** are lowest and are comparable to those for aniline and acetonitrile. The highest value of  $\beta$  among the group 4 complexes is found for **4b** and is similar to that of pyridine.<sup>53</sup>

**UV/Visible Spectroscopic Studies.** Complex **4a** possesses a measurable chromophore at 428 nm which undergoes a

Table 3. Thermodynamic Parameters and  $\beta$  Values for  $\text{Cp}_2\text{MF}_2$  and  $\text{Cp}^*_2\text{MF}_2$  ( $\text{M} = \text{Ti, Zr, Hf}$ )<sup>a,c</sup>

$\text{Cp}_2\text{MF}_2$	HFIP in $\text{CH}_2\text{Cl}_2$		4-fluorophenol in $\text{CH}_2\text{Cl}_2$				$\beta^b$
	$K_{300}$ ( $\text{M}^{-1}$ )	$\Delta\delta_{300\text{K}}^{\text{fit}}$	$K_{300}$ ( $\text{M}^{-1}$ )	$\Delta H^0$ ( $\text{kJ mol}^{-1}$ )	$\Delta S^0$ ( $\text{J mol}^{-1} \text{K}^{-1}$ )	$\Delta\delta_{300\text{K}}^{\text{fit}}$	
4a $\text{Cp}_2\text{TiF}_2$	$9.6 \pm 0.2$	−60.6	$4.6 \pm 0.1$	$-10.9 \pm 0.3$	$-24 \pm 2$	−48.4	5.8
5a $\text{Cp}_2\text{ZrF}_2$	$3.8 \pm 0.1$	−37.2	$1.7 \pm 0.1$	$-13.6 \pm 0.7$	$-41 \pm 3$	−30.4	4.7
6a $\text{Cp}_2\text{HfF}_2$	$3.3 \pm 0.1$	−27.3	$1.7 \pm 0.1$	$-11.8 \pm 0.4$	$-35 \pm 2$	−19.2	4.7
$\text{Cp}^*_2\text{MF}_2$	indole in toluene		4-fluorophenol in toluene				$\beta^b$
	$K_{300}$ ( $\text{M}^{-1}$ )	$\Delta\delta_{300\text{K}}^{\text{fit}}$	$K_{300}$ ( $\text{M}^{-1}$ )	$\Delta H^0$ ( $\text{kJ mol}^{-1}$ )	$\Delta S^0$ ( $\text{J mol}^{-1} \text{K}^{-1}$ )	$\Delta\delta_{300\text{K}}^{\text{fit}}$	
4b $\text{Cp}^*_2\text{TiF}_2$	$5.4 \pm 0.3$	−30.2	$23.1 \pm 0.3$	$-15.9 \pm 0.4$	$-27 \pm 2$	−47.2	6.9
5b $\text{Cp}^*_2\text{ZrF}_2$	$1.4 \pm 0.1$	−19.6	$5.9 \pm 0.4$	$-15.4 \pm 0.5$	$-36 \pm 2$	−31.9	5.6
6b $\text{Cp}^*_2\text{HfF}_2$	$1.4 \pm 0.1$	−12.4	$3.9 \pm 0.1$	$-15.8 \pm 0.5$	$-41 \pm 2$	−25.0	5.4
HFIP in toluene							$\beta$
6b $\text{Cp}^*_2\text{HfF}_2$			$5.5 \pm 0.1$	$-12.2 \pm 0.2$	$-27 \pm 1$	−36.3	5.1

<sup>a</sup>Errors at the 95% confidence level of the fitting routines. <sup>b</sup>Average of values derived from the two H-bond donors. The difference between the determinations was typically less than 0.2 and never exceeded 0.7. In order to ensure comparability of  $\beta$  values for 4b, 5b, and 6b, the data for 6b + HFIP were not included. <sup>c</sup>Solvent values used.  $\text{CH}_2\text{Cl}_2$ :  $\alpha_s = 1.9$ ,  $\beta_s = 1.1$ . Toluene:  $\alpha_s = 1.0$ ,  $\beta_s = 2.2$ .

bathochromic shift upon titration with 4-fluorophenol at 298 K in 1,1,2,2-tetrachloroethane. Therefore, UV/visible spectroscopic titrations were undertaken following the change in absorbance at 450, 460, and 470 nm, giving  $K_{298} = 2.3 \pm 0.8$  and  $\beta = 5.6$  (Table 4, Figure 4) in good agreement with

Table 4. Association Constants and  $\beta$  Values for 4a and 4b with 4-Fluorophenol from UV/vis Titrations<sup>a,b</sup>

	$K_{298}$ ( $\text{M}^{-1}$ )	$\beta$
4a $\text{Cp}_2\text{TiF}_2$ :tetrachloroethane	$2.3 \pm 0.8$	5.6
4b $\text{Cp}^*_2\text{TiF}_2$ :toluene	$27 \pm 4$	7.1

<sup>a</sup>Errors determined by repetition. <sup>b</sup>Here  $\beta$  values are calculated solely from UV/visible titration data assuming  $\alpha_s = 2.0$  and  $\beta_s = 1.3$  for tetrachloroethane and  $\alpha_s = 1.0$  and  $\beta_s = 2.2$  for toluene.<sup>52</sup>

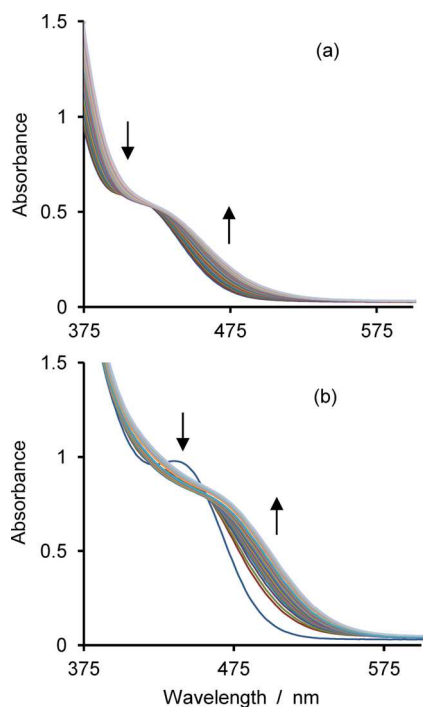


Figure 4. UV/vis spectra for titrations of 4-fluorophenol into (a) a 4.2 mM solution of 4a in tetrachloroethane at 298 K and (b) a 3.3 mM solution of 4b in toluene at 298 K.

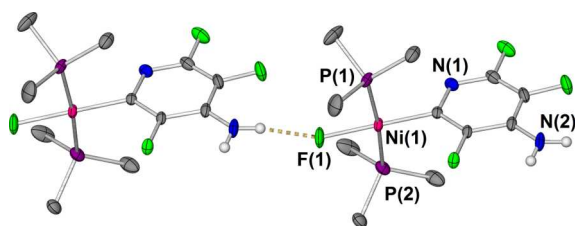
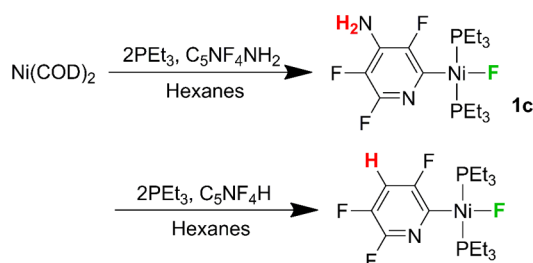
$\beta$  obtained by NMR titration in dichloromethane (5.8).<sup>66</sup> We also observed a color change for 4b ( $\lambda_{\text{max}} = 416$  nm in toluene at 298 K) upon addition of 4-fluorophenol. Binding curves were obtained by UV/vis absorbance measurements at 480, 490, and 500 nm as a function of 4-fluorophenol concentration (Table 4, Figure 4). Fits of the resulting data yielded  $K_{298} = 27 \pm 4$  and  $\beta = 7.1$ , close to the  $\beta$  calculated from NMR spectroscopy.

**X-ray Diffraction Study of Hydrogen Bonding to Nickel Fluoride Complexes.** The high value of  $\beta$  determined for the group 10 complexes suggests that it should be possible to design H-bonded assemblies on the basis of these complexes. Studies directly comparing solution-state interaction energies with crystallographically determined solid-state bond lengths are rare. Those adducts prone to crystallization often lack a measurable binding parameter, while those adducts designed for solution measurement commonly elude cocrystallization. A strategy to counteract the difficulties of cocrystallizing a donor and an acceptor is to design “self-complementary” molecules that possess both donor and acceptor sites.<sup>67</sup> The aim of such bifunctional molecules is the assembly of molecules in a head-to-tail fashion where the donor of one molecule binds to the acceptor of another and the chain propagates indefinitely in the solid state.

The facile synthesis of 1a, *trans*-[Ni(F)(2- $\text{C}_5\text{F}_4\text{N}$ )( $\text{PEt}_3$ )<sub>2</sub>], by a C–F activation step of pentafluoropyridine suggested that this pathway may be open to heteroarene modification. To this end, 4-amino-2,3,5,6-tetrafluoropyridine was investigated: a partially fluorinated heteroarene containing a H-bond donor moiety. Rewardingly, addition of 4-amino-2,3,5,6-tetrafluoropyridine to  $\text{Ni}(\text{PEt}_3)_2$  yielded *trans*-[Ni(F){ $\text{C}_5\text{NF}_3(\text{NH}_2)$ }( $\text{PEt}_3$ )<sub>2</sub>], 1c, and upon workup gave crystals amenable to study by single crystal X-ray diffraction techniques (Scheme 1 and Figure 5). The structure of 1c shows the C–F activated product with the amino functional group evidently tolerated. The amino hydrogens were located directly from the electron density difference map, revealing that one of these hydrogens forms a hydrogen bond to the nickel fluoride ( $\text{H}\cdots\text{F}$  1.87 Å,  $\text{N}\cdots\text{F}$  2.694(2) Å,  $\text{H}\cdots\text{F}-\text{Ni}$  158.1°,  $\text{N}-\text{H}\cdots\text{F}$  166.7°) to generate a 1D hydrogen-bonded polymer. The H-bond geometry has been derived by extending the N–H to typical neutron diffraction values (N–H 1.01 Å) by moving the H atom along the N–H vector.<sup>68</sup>



**Scheme 1.** Synthesis of **1c** and *trans*-[Ni(F)(C<sub>5</sub>NHF<sub>3</sub>)(PEt<sub>3</sub>)<sub>2</sub>]



**Figure 5.** X-ray crystal structure of **1c** highlighting the intermolecular H-bonding between neighboring molecules. Hydrogen atoms, excluding those of the NH<sub>2</sub> moiety, and methyl carbons are omitted for clarity. Ellipsoids shown at the 50% level. Bond lengths (Å): Ni–C(1) 1.864(2), Ni–F(1) 1.872(1), Ni–P(1) 2.1897(5), Ni–P(2) 2.1880(5), H···F 1.701, N···F 2.694(2). Bond angles (deg): P(1)–Ni–P(2) 173.70 (2), C(1)–Ni–F(1) 178.60(7), H···F–Ni 158.1, N–H···F 166.7.

A similar example of a self-complementary complex is found in the related compound *trans*-[Ni(F)(C<sub>5</sub>NHF<sub>3</sub>)(PEt<sub>3</sub>)<sub>2</sub>] reported by Perutz et al. (Scheme 1).<sup>56</sup> Here the C–H bond on the arene skeleton acts as a H-bond donor, albeit a far weaker one than the N–H group in **1c**. In the solid state, an extended structure is formed in *trans*-[Ni(F)(C<sub>5</sub>NHF<sub>3</sub>)(PEt<sub>3</sub>)<sub>2</sub>] by contacts between the Ni–F group of one molecule and the C–H group of the next molecule (C···F 3.007(4) Å). Comparison of the structures of **1c** and *trans*-[Ni(F)(C<sub>5</sub>NHF<sub>3</sub>)(PEt<sub>3</sub>)<sub>2</sub>] reveals a slightly longer Ni–F bond in the former (1.872(1) vs 1.856(2) Å) and a shorter H···F distance<sup>69</sup> (1.701 vs 1.929 Å), consistent with stronger hydrogen bonding in **1c**. The angles at the hydrogen bonds are comparable to one another in the two complexes: **1c** (H···F–Ni 158.1°, N–H···F 166.7°), *trans*-[Ni(F)(C<sub>5</sub>NHF<sub>3</sub>)(PEt<sub>3</sub>)<sub>2</sub>] (H···F–Ni 141.9°, C–H···F 173.1°). The H-bond structure has been derived similarly to that above with C–H 1.083 Å.<sup>68</sup> For comparison, the F···O hydrogen-bond distance in *trans*-[Pd(F)(C<sub>5</sub>NF<sub>4</sub>)(PCy<sub>3</sub>)<sub>2</sub>]·H<sub>2</sub>O is 2.601(6) Å.<sup>42</sup>

The structure of **1c** presented the opportunity to compare the solid-state hydrogen bonding in **1c** to a suitable solution-state analogue. Therefore, we pursued the titration of the individual functionalities of nickel fluoride and amino group in the form of **1a** against 4-amino-2,3,5,6-tetrafluoropyridine. The association constant was determined to be 37.9 ± 0.7 M<sup>−1</sup>, within the range of the N–H hydrogen-bond donors studied (Table 1). This measurement serves as a reference point between solution and solid state.

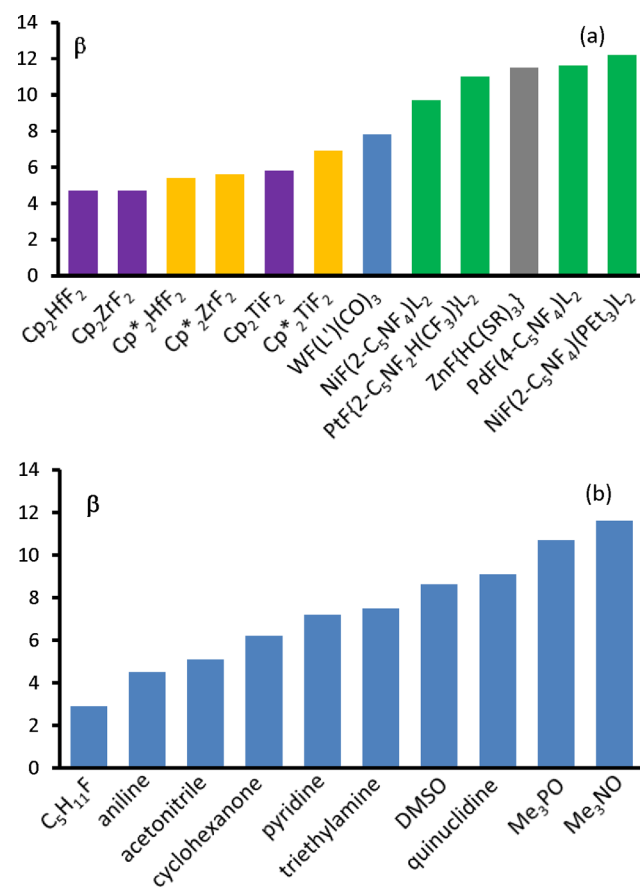
## DISCUSSION

The group 10 metal fluoride complexes, **1a**, **1b**, **2**, and **3**, have proved to be powerful H-bond acceptors, comparable to trimethylamine-*N*-oxide and stronger than trimethylphosphine oxide according to the Hunter scale, with the largest value of

$\beta$  found for the nickel complex **1a**. The stronger H-bond acceptor character of the group 10 monofluorides relative to those of the group 4 difluorides is clearly apparent in the  $\beta$  values. Among the group 4 difluorides, the trends in  $\beta$  follow the sequences **4a** > **5a** ~ **6a** and **4b** > **5b** ~ **6b**. The solvent media for titrations of **1a** and **4b** with 4-fluorophenol are identical, yet the  $K_{300}$  value for **1a** (2800 ± 100) is 2 orders of magnitude greater than that of **4b** (23.1 ± 0.3).

Chart 3 provides a histogram of  $\beta$  values determined in this paper together with a histogram of  $\beta$  values of common organic

**Chart 3.** (a) Histogram of  $\beta$  values for transition metal fluorides in ascending order and colored by group. L = PCy<sub>3</sub>, L' =  $\kappa^3$ -C<sub>3</sub>N<sub>3</sub>N-(C<sub>6</sub>H<sub>4</sub>)C(H)N(CH<sub>2</sub>)<sub>2</sub>NMe<sub>2</sub>, R = 2-pyridyl. Color coding: Cp<sub>2</sub>MF<sub>2</sub> purple, Cp\*<sub>2</sub>MF<sub>2</sub> orange, group 6 fluoride blue, group 10 fluorides green, group 12 fluoride grey. Values of  $\beta$  for Zn and W compounds are calculated from reported association constants.<sup>33,37,70</sup> (b) Histogram of  $\beta$  for organic H-bond acceptors. Values from ref 53 and from calculation (Me<sub>3</sub>NO).



hydrogen bond acceptors. The compounds W(F){ $\kappa^3$ -C<sub>3</sub>N<sub>3</sub>N-(C<sub>6</sub>H<sub>4</sub>)C(H)N(CH<sub>2</sub>)<sub>2</sub>NMe<sub>2</sub>}(CO)<sub>3</sub> and tris(2-pyridylthio)-methyl zinc fluoride are also included with their  $\beta$  values calculated from literature association constants<sup>33,37</sup> (tungsten fluoride with 4-chlorophenol  $K_{300}$  = 32 M<sup>−1</sup> (CH<sub>2</sub>Cl<sub>2</sub>) and 330 M<sup>−1</sup> (toluene); zinc fluoride with indole  $K_{300}$  = 85 M<sup>−1</sup>). The tungsten fluoride has an intermediate  $\beta$  value (7.8), whereas the zinc fluoride is comparable to **1a** in terms of  $\beta$  (ZnF 11.5, **1a** 12.1 ± 1.0).

Trends in enthalpies of binding of 4-fluorophenol again illustrate that the binding of group 10 fluorides is much



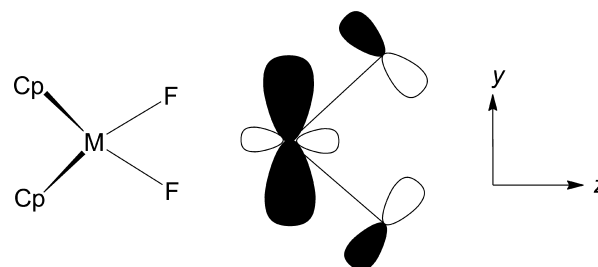
stronger than that for group 4 fluorides (see Chart S1). There is less variation between the enthalpies of the group 4 compounds than is found in their  $\ln K_{300}$  values. The group 10 compounds show significant variations in their enthalpies and particularly large variations in entropy down the group, as we found for halogen bonding.<sup>55</sup> The origin of the changes in entropy is not understood. Laurence uses the binding enthalpy of 4-fluorophenol in  $\text{CCl}_4$  solution as the best key measurement for his scale of hydrogen bonding.<sup>51</sup> We therefore conducted measurements on **1a** in  $\text{CCl}_4$  and found that the best comparator for **1a** in terms of H-bond enthalpy is THF ( $\Delta H -23.7 \text{ kJ mol}^{-1}$ ).

A major determinant of the strength of hydrogen bonding to metal fluoride complexes is certainly the polarity of the M–F bond. The ionic character of the  $\sigma$ -component of the bond depends on the electronegativity differences between the elements. However, the overall polarity of metal fluoride complexes also depends on the extent of ligand-to-metal  $\pi$ -donation ( $d\pi$ – $p\pi$  interactions). The electronegativity difference between the metals and fluorine decreases from group 4 to group 10; zirconium and hafnium are slightly less electronegative than titanium, whereas palladium and platinum are more electronegative than nickel.<sup>71</sup> Although fluorine has been argued to be the strongest  $\pi$ -donor of the halides,<sup>72</sup> the  $d\pi$ – $p\pi$  interactions require a vacant acceptor orbital on the metal of the right symmetry. If these d-orbitals are full as in  $d^8$  square planar complexes, the  $d\pi$ – $p\pi$  interactions are repulsive. Only strong push–pull effects can mitigate this repulsion.<sup>73</sup> In our earlier paper, we reported calculations on models of **1** and **3**, and showed that the electrostatic potential minimum along the extension of the M–F vector is slightly deeper for platinum fluoride than for nickel fluoride, consistent with stronger halogen and hydrogen bonding.<sup>55</sup> A comparison of metal-fluoride bonding in  $\text{M}(\text{H}_2\text{PCH}_2\text{CH}_2\text{PH}_2)(\text{C}_6\text{F}_5)\text{F}$  ( $\text{M} = \text{Ni}, \text{Pt}$ ) highlighted the role of  $d\pi$ – $p\pi$  repulsion and indicated that these interactions weakened the Pt–F bond relative to Ni–F.<sup>74</sup> Mezzetti and Becker questioned the importance of push–pull effects and emphasized the ionic character of the M–F bond, writing “ $d^6$  and  $d^8$  fluoro complexes are generally labile and highly reactive towards nucleophiles in view of the significant ionic character of the M–F bond and of the hard/soft mismatch, unless some kind of stabilizing interaction is operative”.<sup>75</sup> In keeping with this statement, the fluoride ligand in **1a** is very easily displaced by other halides.<sup>38e</sup> Holland et al. also emphasized that properties of late transition metal fluorides can be understood by a “polarization” model with little recourse to  $d\pi$ – $p\pi$  interactions.<sup>76</sup> In a recent study of nickel and palladium pincer complexes  $\text{M}(\text{iprPCP})\text{X}$  with a wide variety of X ligands, it was shown that the chemical shift  $\delta^{13}\text{C}(\text{ipso})$  provides a measure of  $\sigma$ -bond strength while the difference in chemical shifts  $\delta^{13}\text{C}(\text{para}) - \delta^{13}\text{C}(\text{meta})$  probes  $\pi$ -bonding. On these measures, fluoride was a very weak  $\sigma$ -binder but exhibited appreciable  $\pi$ -bonding.<sup>77</sup> Nickel analogues with other pincer ligands behaved similarly.<sup>41e</sup> The results reported in the present paper provide a much more quantitative indicator of ionic character in the M–F bond of the  $d^8$  complexes than previous approaches, though this does not exclude four-electron  $d\pi$ – $p\pi$  repulsions. Within the group 10 series with  $\text{PCy}_3$  ligands, the measures of H-bonding strength reach a maximum for palladium, when measured both as  $\beta$  (derived from  $K_{300}$ ) and as  $-\Delta H^0$ .<sup>78</sup>

The lower H-bond strength of the group 4  $\text{Cp}_2\text{MF}_2$  and  $\text{Cp}^*\text{MF}_2$  complexes compared to the  $d^8$  complexes is

inconsistent with electronegativity difference as the principal determinant. Rather, in  $\text{Cp}_2\text{MF}_2$ , the metal has a  $d^0$  configuration and there is an unoccupied MO ( $a_1, d_{yz}$ ) capable of drawing electron density away from the fluorides by interaction with the  $a_1$  combination of their in-plane  $p_\pi$  orbitals (Scheme 2),<sup>79</sup>

**Scheme 2.** Overlap of the  $a_1$  Combination of F( $2p_\pi$ ) Orbitals and the Metal  $d_{yz}$  Orbital of  $\text{Cp}_2\text{MF}_2$  Adapted from ref 79a



thereby reducing the H-bond acceptor capability of the fluoride ligands. The  $b_2$  out-of-phase combination of the in-plane F  $p_\pi$  orbitals can interact with the  $d_{yz}$  ( $b_2$ ) orbital on the metal in principle, but the overlap is likely to be low, since the F–M–F angles are close to  $90^\circ$ .<sup>80</sup> It is unsurprising that the H-bond strengths of  $\text{Cp}^*\text{MF}_2$  complexes with 4-fluorophenol are greater than those of  $\text{Cp}_2\text{MF}_2$ , as the  $\text{Cp}^*$  ligand supplies more electron density. The observation that the H-bond strength of the Ti complexes exceeds those of the Zr and Hf analogues is once again inconsistent with simple electronegativity considerations, and provides experimental evidence for increased ionic character for Ti.

The exceptional strength of the hydrogen bonds to group 10 metal fluoride complexes suggests that they may be excellent building blocks for forming assemblies linked by H-bonds. The synthesis of the amino-substituted nickel complex *trans*- $[\text{Ni}(\text{F})\{\text{C}_5\text{NF}_3(\text{NH}_2)\}(\text{PEt}_3)_2]$ , **1c**, exploits the tolerance of the C–F activation reaction to additional functionalities. The crystal structure of **1c** illustrates self-complementary hydrogen bonding and provides details of the H-bonding geometry. There is potential to make use of this motif with other metal fluoride complexes, just as has been done in halogen bonding studies with other metal halides.<sup>67</sup>

## CONCLUSION

In this paper, we have quantified H-bond acceptor strength and hence Lewis basicity of metal fluorides. We have shown that group 10 metal fluorides exhibit exceptionally strong H-bond acceptor character, with the nickel fluoride **1a** and the palladium fluoride **2** of the  $\text{PCy}_3$  series having the highest association constants. We derive values of the solvent-independent H-bond acceptor parameter  $\beta$  from these measurements, allowing comparison to organic H-bond acceptors. The group 10 fluorides **1a**–**3** are comparable to or even exceed in strength some of the strongest of such H-bond acceptors such as trimethylphosphine oxide and trimethylamine-*N*-oxide. Their great strength provides direct evidence of the polarity of the M–F bonds. We have also measured the strength of halogen bonds from  $\text{C}_6\text{F}_5\text{I}$  with the same H-bond acceptors and find that these halogen bonds are comparable in strength to the weakest of the hydrogen bonds that we have examined, such as to pyrrole. In comparison to the group 10 monofluorides, the group 4 difluorides **4a**–**6b** examined are weaker H-bond acceptors. The series of  $K_{300}$  and  $\beta$  follows the

trend  $\text{Ti} > \text{Zr} \sim \text{Hf}$  with a value of  $\beta$  comparable to that of pyridine for  $\text{Cp}^*_2\text{TiF}_2$  going down to a value similar to that of aniline for  $\text{Cp}_2\text{ZrF}_2$ . The  $\text{Cp}^*$  compounds display stronger H-bond acceptor power than their Cp counterparts, as would be expected due to the electron releasing nature of  $\text{Cp}^*$ . There is no evidence for steric encumbrance by  $\text{Cp}^*$  relative to Cp, but the smaller association constant for **1b** which has a  $\text{PCy}_3$  ligand than that for **1a** ( $\text{PEt}_3$  ligand) suggests a steric effect. Unlike **1a–3**, compounds **4a–6b** possess vacant d-orbitals capable of  $\pi$ -interaction with the fluoride ligands; this overlap undoubtedly contributes to the reduced H-bond acceptor strength of **4a–6b**. This evidence for the high polarity of metal fluoride bonds provides a definitive conclusion to controversies in the older literature about the nature of the transition-metal–fluorine bond. Finally, the strong H-bond to late transition-metal fluorides shows their potential as building blocks for H-bonded assemblies and networks, as shown in the self-complementary amine-substituted complex **1c** which exhibits a chain structure with  $\text{N–H}\cdots\text{F–Ni}$  hydrogen bonds.

## EXPERIMENTAL SECTION

**General Procedures.** All operations were performed under an argon atmosphere, either on standard Schlenk lines ( $10^{-2}$  mbar) or in a glovebox. Solvents were dried and distilled over sodium (toluene) or  $\text{CaH}_2$  (dichloromethane and carbon tetrachloride), stored under Ar in ampules fitted with J. Young's PTFE stopcocks, and degassed prior to use. Pyrrole was degassed and dried on 3 Å molecular sieves.

All NMR spectra were recorded on Bruker AMX500 spectrometers. All  $^1\text{H}$  NMR spectra were recorded at 500.2 MHz; chemical shifts are reported in ppm ( $\delta$ ) relative to tetramethylsilane and are referenced using the chemical shifts of residual protio solvent resonances (benzene,  $\delta$  7.16). The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were recorded at 202.5 MHz and are referenced to external  $\text{H}_3\text{PO}_4$ .  $^{19}\text{F}$  NMR spectra were recorded at 470.5 MHz and referenced to external  $\text{CFCl}_3$  at  $\delta$  0 or internal  $\text{C}_6\text{F}_6$  at  $\delta$  –162.9. The temperature of the probe was calibrated according to published procedures.<sup>81</sup> Mass spectra were recorded by the University of York analytical services on a Waters GCT instrument fitted with a Linden LIFDI probe and are quoted for  $^{58}\text{Ni}$ . Samples for elemental analysis were prepared in a glovebox, sealed under a vacuum, and measured by Elemental Microanalysis Ltd., Okehampton. Chemicals were obtained from Aldrich except for the following: allylpalladium chloride dimer and  $\text{PCy}_3$  from Strem, pentafluoropyridine, 4-amino-2,3,5,6-tetrafluoropyridine, and 2,3,5-trifluoro-4-trifluoromethyl-pyridine from Fluorochem. *trans*- $[\text{Ni}(\text{F})(2\text{-C}_5\text{NF}_4)(\text{PEt}_3)_2]$ ,<sup>56</sup> *trans*- $[\text{Ni}(\text{F})(2\text{-C}_5\text{NF}_4)(\text{PCy}_3)_2]$ ,<sup>55</sup> *trans*- $[\text{Pd}(\text{F})(4\text{-C}_5\text{NF}_4)(\text{PCy}_3)_2]$ ,<sup>42</sup> *trans*- $[\text{Pt}(\text{F})\{2\text{-C}_5\text{NF}_2\text{H}(\text{CF}_3)\}(\text{PCy}_3)_2]$ ,<sup>82</sup>  $\text{Cp}^*_2\text{TiF}_2$ ,<sup>83</sup>  $\text{Cp}^*_2\text{MF}_2$  ( $\text{M} = \text{Zr}, \text{Hf}$ ),<sup>83</sup>  $\text{Cp}_2\text{TiF}_2$ ,<sup>84</sup> and  $\text{Cp}_2\text{MF}_2$  ( $\text{M} = \text{Zr}, \text{Hf}$ )<sup>85</sup> were synthesized according to literature procedures.

**Synthesis of *trans*- $[\text{Ni}(\text{F})\{2\text{-C}_5\text{NF}_3(\text{NH}_2)\}(\text{PEt}_3)_2]$  (**1c**).** To a suspension of  $\text{Ni}(\text{COD})_2$  (100 mg, 0.36 mmol) in hexane was added triethylphosphine (100 mg, 0.85 mmol), giving a red solution. Addition of a benzene solution of 4-aminotetrafluoropyridine (65 mg, 0.39 mmol) with 1 h of stirring gave a yellow powder. The powder was isolated by filtration, washed with hexane, and then recrystallized twice from THF/hexane to give a yellow crystalline solid (40 mg, 9%).

$^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  1.10 (18H, m,  $\text{CH}_3$ ), 1.24 (6H, m,  $\text{CH}_2$ ), 1.30 (6H, m,  $\text{CH}_2$ ), 3.32 (2H, s,  $\text{NH}_2$ ).  $^1\text{H}\{^{31}\text{P}\}$  NMR:  $\delta$  1.10 (18H, quintet,  $J = 7$  Hz,  $\text{CH}_3$ ), otherwise as for  $^1\text{H}$  NMR.  $^{19}\text{F}$  NMR (470 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  –92.1 (1F, dd,  $J = 29$ ,  $J = 29$  Hz), –135.5 (1F, d,  $J_{\text{FF}} = 29$  Hz), –175.2 (1F, dm,  $J_{\text{FF}} = 30$  Hz), –367.6 (1F, t,  $J_{\text{FP}} = 47$  Hz).  $^{31}\text{P}$  NMR (202 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  12.6 (d,  $J_{\text{FP}} = 47$  Hz). LIFDI  $m/z$ : calcd, 460.1330 (100.0%); found, 460.1372 (100.0%  $\text{M}^+$ ). Anal. Calcd for  $\text{C}_{17}\text{H}_{32}\text{F}_4\text{N}_2\text{NiP}_2$ : C, 44.28; H, 7.00; N, 6.08. Found C, 44.03; H, 6.82; N, 5.98.

**NMR Titrations and Analysis of Data.** The equilibrium constants were determined through NMR titration at a series of temperatures, by following the  $^{19}\text{F}$  chemical shift of the fluoride ligand

coordinated to the transition metal. The  $^{19}\text{F}$  NMR spectra were collected unlocked. However, for each temperature, the spectrometer was shimmed with a solution of the corresponding metal fluoride in either toluene- $d_8$  (for toluene titrations) or chloroform- $d$  (for dichloromethane and carbon tetrachloride titrations) and maintained with the same settings throughout. The volumes of the solutions were assumed to be the sum of the volumes of the components, thereby enabling the densities of the solutions to be calculated. The activities of the species were assumed equal to their molar concentration. The calculations for the equilibrium constants were carried out with Microsoft Excel, using a macro programmed by C. A. Hunter. There are two parameters to be fitted: the equilibrium constant  $K$  and the shift from the signal of free metal fluoride for the coordinated fluoride in the adduct,  $\Delta\delta_{\text{F}}$ . The two parameters can be fitted for the whole range of temperatures without any restraints.  $\Delta H^\circ$  and  $\Delta S^\circ$  were calculated from the van't Hoff plots of the equilibrium constants.

### General Procedure for the Preparation of the NMR Samples.

Stock solutions were prepared by recording the masses of the host, guest, and solvent added. To NMR tubes fitted with Young's taps in a glovebox was added approximately 400  $\mu\text{L}$  of host stock solution and the accurate mass recorded to allow a determination of the number of moles of host in the sample. Similarly, the guest stock solution was added by syringe and the mass of the addition recorded. To standardize the volume of the samples, solvent was added to give a volume of 600  $\mu\text{L}$ . Details of the composition of stock solutions are provided in Tables S1–S5. The  $^{19}\text{F}$  NMR spectra of all samples were recorded at various temperatures. The samples were kept in a bath close to the temperature of the probe and left to equilibrate inside the probe for 2 min before the spectrum was recorded.

**X-ray Crystallography.** Diffraction data for **1c** were collected at 110 K on an Agilent SuperNova diffractometer with Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å). Data collection, unit cell determination, and frame integration were carried out with *CrysAlisPro* software. Absorption corrections were applied using crystal face indexing and the *ABSPACK* absorption correction software within *CrysAlisPro*. Structures were solved and refined using *Olex2*<sup>86</sup> implementing *SHELXS-97* and *SHELXL-97* algorithms. All non-hydrogen atoms were refined anisotropically. Carbon-bound hydrogen atoms were placed at calculated positions and refined using a riding model. Hydrogen atoms bound to nitrogen were located directly from the electron density difference map, and their positions and isotropic displacement parameters were refined. Adjustments to the hydrogen bond geometry are not included in the CIF file.

Empirical formula  $\text{C}_{17}\text{H}_{32}\text{F}_4\text{N}_2\text{NiP}_2$ , formula weight 461.10, temperature/K 110.00(10), monoclinic, space group  $\text{P}2_1/c$ ,  $a$  15.0474(5),  $b$  9.60545(18),  $c$  16.7082(5) Å,  $\beta$  112.614(4)°,  $V$  2229.27(13) Å<sup>3</sup>,  $Z = 4$ ,  $\rho_{\text{calc}}$  1.374 mg/mm<sup>3</sup>,  $\mu$  1.050 mm<sup>–1</sup>,  $F(000)$  968.0, crystal size 0.552  $\times$  0.257  $\times$  0.129 mm<sup>3</sup>,  $2\theta$  range for data collection 5.86–64.36°, index ranges  $-22 \leq h \leq 21$ ,  $-14 \leq k \leq 13$ ,  $-24 \leq l \leq 24$ , reflections collected 28647, independent reflections 7276 [ $R(\text{int}) = 0.0332$ ], data/restraints/parameters 7276/0/249, goodness-of-fit on  $F^2$  1.064, final  $R$  indexes [ $I \geq 2\sigma(I)$ ],  $R_1 = 0.0390$ ,  $wR_2 = 0.0889$ , final  $R$  indexes [all data]  $R_1 = 0.0532$ ,  $wR_2 = 0.0960$ . CCDC 1413441.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b07509.

Composition of stock solutions, titration curves and van't Hoff plots, sample  $^{19}\text{F}$  NMR spectra, comparisons of association constants and enthalpies of H-bond formation, NMR spectra of **1c**, electrostatic potential calculations, and UV/vis titration curves (PDF)

X-ray crystallographic data for **1c** (CIF)

## ■ AUTHOR INFORMATION

## Corresponding Authors

\*ch664@cam.ac.uk

\*lee.brammer@sheffield.ac.uk

\*robin.perutz@york.ac.uk

## Present Addresses

<sup>||</sup>D.A.S.: CatSci Ltd., CBTC2, Capital Business Park, Wentloog, Cardiff, CF3 2PX, U.K.<sup>⊥</sup>T.B.: Leibniz Institute for Catalysis at the University of Rostock, Albert-Einstein-Str. 29a, 18059 Rostock, Germany.<sup>#</sup>C.B.: Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany.<sup>∇</sup>R.N.: Department of Chemistry, Kohat University of Science and Technology, Kohat, Khyber Pakhtunkhwa, Pakistan.<sup>○</sup>S.N.: Government College Women's University, Faisalabad, Pakistan.

## Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This work was supported by the EPSRC (EP/J012955/1 and EP/J012998/1), by the Deutsche Forschungsgemeinschaft (research fellowship for T.B., grant no. BE 4370/1-1), by Kohat University of Science and Technology and the Wild Fund of the University of York (studentship to R.N.), and by the International Research Support Initiative Program of the Pakistan Higher Education Commission (PIN IRSIP-5-Ps-08 for S.N.). Professor Robert Crabtree (Yale University) is warmly thanked for helpful discussions.

## ■ REFERENCES

- (1) Natale, D.; Mareque-Rivas, J. C. *Chem. Commun.* **2008**, 425.
- (2) Brammer, L. *Dalton Trans.* **2003**, 3145.
- (3) Perutz, M. F. *Trends Biochem. Sci.* **1989**, 14, 42.
- (4) (a) Phillips, S. E. V.; Schoenborn, B. P. *Nature* **1981**, 292, 81.
- (b) Shaanan, B. *Nature* **1982**, 296, 683.
- (5) Kovaleva, E. G.; Lipscomb, J. D. *Science* **2007**, 316, 453.
- (6) Casadei, C. M.; Gumiero, A.; Metcalfe, C. L.; Murphy, E. J.; Basran, J.; Grazia Concilio, M.; Teixeira, S. C. M.; Schrader, T. E.; Fielding, A. J.; Ostermann, A.; Blakeley, M. P.; Raven, E. L.; Moody, P. C. E. *Science* **2014**, 345, 193.
- (7) Shook, R. L.; Borovik, A. S. *Inorg. Chem.* **2010**, 49, 3646.
- (8) Sheng, Y.; Abreu, I. A.; Cabelli, D. E.; Maroney, M. J.; Miller, A.-F.; Teixeira, M.; Valentine, J. S. *Chem. Rev.* **2014**, 114, 3854.
- (9) Nicolet, Y.; Piras, C.; Legrand, P.; Hatchikan, C. E.; Fontecilla-Camps, J. *Structure* **1999**, 7, 13.
- (10) (a) Migliore, A.; Polizzi, N. F.; Therien, M. J.; Beratan, D. N. *Chem. Rev.* **2014**, 114, 3381. (b) Usharani, D.; Lacy, D. C.; Borovik, A. S.; Shaik, S. J. *Am. Chem. Soc.* **2013**, 135, 17090.
- (11) (a) Baxter, N. J.; Olguin, N. F.; Golicnik, M.; Feng, G.; Hounslow, A. M.; Bermel, W.; Blackburn, G. M.; Hollfelder, F.; Waltho, J. P.; Williams, N. H. *Proc. Natl. Acad. Sci. U. S. A.* **2006**, 103, 14732. (b) Baxter, N. J.; Bowler, M. W.; Alizadeh, T.; Cliff, M. J.; Hounslow, A. M.; Wu, B.; Berkowitz, D. B.; Williams, N. H.; Blackburn, G. M.; Waltho, J. P. *Proc. Natl. Acad. Sci. U. S. A.* **2010**, 107, 4555.
- (12) (a) Das, S.; Brudvig, G. W.; Crabtree, R. H. *Chem. Commun.* **2008**, 413. (b) Schley, N. D.; Halbert, S.; Raynaud, C.; Eisenstein, O.; Crabtree, R. H. *Inorg. Chem.* **2012**, 51, 12313.
- (13) (a) Breit, B.; Gellrich, U.; Li, T.; Lynam, J. M.; Milner, L. M.; Pridmore, N. E.; Slattery, J. M.; Whitwood, A. C. *Dalton Trans.* **2014**, 43, 11277. (b) Chevallier, F.; Breit, B. *Angew. Chem., Int. Ed.* **2006**, 45, 1599. (c) Rummelt, S. M.; Radkowski, K.; Roşca, D.-A.; Fürstner, A. J. *Am. Chem. Soc.* **2015**, 137, 5506.
- (14) Schmeier, T. J.; Dobereiner, G. E.; Crabtree, R. H.; Hazari, N. J. *J. Am. Chem. Soc.* **2011**, 133, 9274.
- (15) (a) Yang, J. Y.; Smith, S. E.; Liu, T.; Dougherty, W. G.; Hoffer, W. A.; Kassel, W. S.; DuBois, M. R.; DuBois, D. L.; Bullock, R. M. J. *Am. Chem. Soc.* **2013**, 135, 9700. (b) O'Hagan, M.; Ho, M.-H.; Yang, J. Y.; Appel, A. M.; DuBois, M. R.; Raugai, S.; Shaw, W. J.; DuBois, D. L.; Bullock, R. M. J. *Am. Chem. Soc.* **2012**, 134, 19409.
- (16) Wakerley, D. W.; Reisner, E. *Phys. Chem. Chem. Phys.* **2014**, 16, 5739.
- (17) McCrory, C. C. L.; Uyeda, C.; Peters, J. C. *J. Am. Chem. Soc.* **2012**, 134, 3164.
- (18) (a) Turkington, J. R.; Bailey, P. J.; Love, J. B.; Wilson, A. M.; Tasker, P. A. *Chem. Commun.* **2013**, 49, 1891. (b) Wilson, A. M.; Bailey, P. J.; Tasker, P. A.; Turkington, J. R.; Grant, R. A.; Love, J. B. *Chem. Soc. Rev.* **2014**, 43, 123.
- (19) (a) Braga, D.; Grepioni, F.; Biradha, K.; Pedireddi, V. R.; Desiraju, G. R. *J. Am. Chem. Soc.* **1995**, 117, 3156. (b) Biradha, K.; Desiraju, G. R.; Braga, D.; Grepioni, F. *Organometallics* **1996**, 15, 1284. (c) Brammer, L.; Bruton, E. A.; Sherwood, P. *New J. Chem.* **1999**, 23, 965. (d) Brammer, L.; Bruton, E. A.; Sherwood, P. *Cryst. Growth Des.* **2001**, 1, 277.
- (20) (a) Burrows, A. D.; Chan, C.-W.; Chowdhry, M. M.; McGrady, J. E.; Mingos, D. M. P. *Chem. Soc. Rev.* **1995**, 24, 329. (b) Aakeröy, C. B.; Beatty, A. M.; Leinen, D. S. *J. Am. Chem. Soc.* **1998**, 120, 7383. (c) Aakeröy, C. B.; Beatty, A. M.; Leinen, D. S. *Angew. Chem., Int. Ed.* **1999**, 38, 1815. (d) Kumar, R. K.; Balasubramanian, S.; Goldberg, I. *Chem. Commun.* **1998**, 1435. (e) Qin, Z. Q.; Jennings, M. C.; Puddephatt, R. J.; Muir, K. W. *CrystEngComm* **2000**, 2, 73. (f) Brammer, L.; Mareque Rivas, J. C.; Atencio, R.; Fang, S.; Pigge, F. C. *J. Chem. Soc., Dalton Trans.* **2000**, 3855. (g) Brammer, L.; Swearingen, J. K.; Bruton, E. A.; Sherwood, P. *Proc. Natl. Acad. Sci. U. S. A.* **2002**, 99, 4956. (h) Dolling, B.; Gillon, A. L.; Orpen, A. G.; Starbuck, J.; Wang, X.-M. *Chem. Commun.* **2001**, 567. (i) Angeloni, A.; Crawford, P. C.; Orpen, A. G.; Podesta, T. J.; Shore, B. J. *Chem. - Eur. J.* **2004**, 10, 3783.
- (21) Ferlay, S.; Holakovský, R.; Hosseini, M. W.; Planeixa, J.-M.; Kyrtsakas, N. *Chem. Commun.* **2003**, 1224.
- (22) (a) Mínguez Espallargas, G.; Hippler, M.; Florence, A. J.; Fernandes, P.; van de Streek, J.; Brunelli, M.; David, W. I. F.; Shankland, K.; Brammer, L. *J. Am. Chem. Soc.* **2007**, 129, 15606. (b) Adams, C. J.; Colquhoun, H. M.; Crawford, P. C.; Lusi, M.; Orpen, A. G. *Angew. Chem., Int. Ed.* **2007**, 46, 1124. (c) Mínguez Espallargas, G.; van de Streek, J.; Fernandes, P.; Florence, A. J.; Brunelli, M.; Shankland, K.; Brammer, L. *Angew. Chem., Int. Ed.* **2010**, 49, 8892.
- (23) Emsley, J. *Chem. Soc. Rev.* **1980**, 9, 91.
- (24) Yandulov, D. V.; Caulton, K. G.; Belkova, N. V.; Shubina, E. S.; Epstein, L. M.; Khoroshum, D. V.; Musaev, D. G.; Morokuma, K. *J. Am. Chem. Soc.* **1998**, 120, 12553.
- (25) Mínguez Espallargas, G.; Zordan, F.; Arroyo Marin, L.; Adams, H.; Shankland, K.; van de Streek, J.; Brammer, L. *Chem. - Eur. J.* **2009**, 15, 7554.
- (26) Belkova, N. V.; Shubina, E. S.; Epstein, L. M. *Acc. Chem. Res.* **2005**, 38, 624.
- (27) (a) Filippov, O. A.; Belkova, N. V.; Epstein, L. M.; Shubina, E. S. *J. Organomet. Chem.* **2013**, 747, 30. (b) Filippov, O. A.; Belkova, N. V.; Epstein, L. M.; Lledos, A.; Shubina, E. S. *ChemPhysChem* **2012**, 13, 2677.
- (28) Siegbahn, P. E. M.; Eisenstein, O.; Rheingold, A. L.; Koetzle, T. F. *Acc. Chem. Res.* **1996**, 29, 348.
- (29) Peris, E.; Lee, J. C., Jr.; Rambo, J. R.; Eisenstein, O.; Crabtree, R. H. *J. Am. Chem. Soc.* **1995**, 117, 3485.
- (30) (a) Albeniz, A. C.; Casares, J. C. *Adv. Organomet. Chem.* **2014**, 62, 1. (b) Vigalok, A. *Organometallics* **2011**, 30, 4802. (c) Campbell, M. G.; Ritter, T. *Chem. Rev.* **2015**, 115, 612. (d) Engle, K. M.; Mei, T.-S.; Wang, X.; Yu, J.-Q. *Angew. Chem., Int. Ed.* **2011**, 50, 1478. (e) Watson, D. A.; Su, M.; Teverovskiy, G.; Zhang, Y.; Garcia-Fortanet, J.; Kinzel, T.; Buchwald, S. L. *Science* **2009**, 325, 1661.
- (31) (a) Clot, E.; Eisenstein, O.; Jasim, N.; Macgregor, S. A.; McGrady, J. E.; Perutz, R. N. *Acc. Chem. Res.* **2011**, 44, 333.



- (b) Weaver, J.; Senaweera, S. *Tetrahedron* **2014**, *70*, 7413. (c) Ahrens, T.; Kohlmann, J.; Ahrens, M.; Braun, T. *Chem. Rev.* **2015**, *115*, 931. (d) Amii, H.; Uneyama, K. *Chem. Rev.* **2009**, *109*, 2119.
- (32) (a) Chierotti, M. R.; Rossin, M.; Gobetto, R.; Peruzzini, M. *Inorg. Chem.* **2013**, *52*, 12616. (b) Dubinsky-Davidchik, I. S.; Potash, S.; Goldberg, I.; Vigalok, A.; Vedernikov, A. N. *J. Am. Chem. Soc.* **2012**, *134*, 14027. (c) Kaspi, A.; Yahav-Levi, A.; Goldberg, I.; Vigalok, A. *Inorg. Chem.* **2008**, *47*, 5. (d) Laitar, D. S.; Müller, P.; Gray, T. G.; Sadighi, J. P. *Organometallics* **2005**, *24*, 4503. (e) Macgregor, S. A.; Roe, D. C.; Marshall, W. J.; Bloch, K. M.; Bakhmutov, V. I.; Grushin, V. V. *J. Am. Chem. Soc.* **2005**, *127*, 15304. (f) Reade, S. P.; Nama, D.; Mahon, M. F.; Pregosin, P. S.; Whittlesey, M. K. *Organometallics* **2007**, *26*, 3484. (g) Maity, A.; Stanek, R. J.; Naderson, B. L.; Zeller, M.; Hunter, A. D.; Moore, C. E.; Rheingold, A. I.; Gray, T. G. *Organometallics* **2015**, *34*, 109.
- (33) Richmond, T. G. *Coord. Chem. Rev.* **1990**, *105*, 221.
- (34) Osterberg, C. E.; King, M. A.; Arif, A. M.; Richmond, T. G. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 888.
- (35) We note that for the tantalum fluoride salt  $[\text{Et}_3\text{NH}][\text{Cp}^*\text{TaF}_6]$  the dissociation constant of the ion-pair has been reported to be  $2.3 \times 10^{-2} \text{ M}^{-1}$ . However, the charged nature of the metal fluoride in this case precludes a direct comparison to the uncharged compounds of our study. Shin, J. H.; Parkin, G. *Organometallics* **1998**, *17*, 5689.
- (36) Libri, S.; Jasim, N. A.; Perutz, R. N.; Brammer, L. *J. Am. Chem. Soc.* **2008**, *130*, 7842.
- (37) Sattler, W.; Ruccolo, S.; Parkin, G. *J. Am. Chem. Soc.* **2013**, *135*, 18714.
- (38) (a) Jasim, N. A.; Perutz, R. N.; Foxon, S. P.; Walton, P. H. *J. Chem. Soc., Dalton Trans.* **2001**, 1676. (b) Jasim, N. A.; Perutz, R. N. *J. Am. Chem. Soc.* **2000**, *122*, 8685. (c) Whittlesey, M. K.; Perutz, R. N.; Greener, B.; Moore, M. H. *Chem. Commun.* **1997**, 187. (d) Braun, T.; Foxon, S. P.; Perutz, R. N.; Walton, P. H. *Angew. Chem., Int. Ed.* **1999**, *38*, 3326. (e) Archibald, S. J.; Braun, T.; Gaunt, J. A.; Hobson, J. E.; Perutz, R. N. *J. Chem. Soc., Dalton Trans.* **2000**, 1013. (f) Procacci, B.; Jiao, Y.; Evans, M. E.; Jones, W. D.; Perutz, R. N.; Whitwood, A. C. *J. Am. Chem. Soc.* **2015**, *137*, 1258.
- (39) (a) Bramanathan, N.; Carmona, M.; Lowe, J. P.; Mahon, M. F.; Poulten, R. C.; Whittlesey, M. K. *Organometallics* **2014**, *33*, 1986. (b) Segarra, S.; Mas-Marzá, E.; Lowe, J. P.; Mahon, M. F.; Poulten, R. C.; Whittlesey, M. K. *Organometallics* **2012**, *31*, 8584.
- (40) (a) Murphy, V. J.; Hascall, T.; Chen, J. Y.; Parkin, G. *J. Am. Chem. Soc.* **1996**, *118*, 7428. (b) Murphy, D.; Rabinovich, V. J.; Hascall, T.; Klooster, W. T.; Koetzle, T. F.; Parkin, G. *J. Am. Chem. Soc.* **1998**, *120*, 4372.
- (41) (a) Roe, D. C.; Marshall, W. J.; Davidson, F.; Soper, P. D.; Grushin, V. V. *Organometallics* **2000**, *19*, 4575. (b) Gil-Rubio, J.; Werberdörfer, B.; Werner, J. *J. Chem. Soc., Dalton Trans.* **1999**, 1437. (c) Ball, N. D.; Sanford, M. S. *J. Am. Chem. Soc.* **2009**, *131*, 3796. (d) Manson, J. L.; Warter, M. L.; Schlueter, J. A.; Lancaster, T.; Steele, A. J.; Blundell, S. J.; Pratt, F. L.; Singleton, J.; McDonald, R. D.; Lee, C.; Whangbo, M. H.; Plonczak, A. *Angew. Chem., Int. Ed.* **2011**, *50*, 1573. (e) Vabre, B.; Petiot, P.; Declercq, R.; Zargarian, D. *Organometallics* **2014**, *33*, 5173. (f) Li, W.; Kiran, M. S. R. N.; Manson, J. L.; Schlueter, J. A.; Thirumurugan, J.; Ramamurthy, U.; Cheetham, A. K. *Chem. Commun.* **2013**, *49*, 4471. (g) Truscott, B. J.; Nahra, F.; Slawin, A. M. Z.; Cordes, D. B.; Nolan, S. P. *Chem. Commun.* **2015**, *51*, 62.
- (42) Jasim, N. A.; Perutz, R. N.; Whitwood, A. C.; Braun, T.; Izundu, J.; Neumann, B.; Rothfeld, S.; Stammer, H. G. *Organometallics* **2004**, *23*, 6140.
- (43) Emsley, J.; Reza, N. M.; Dawes, H. M.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1986**, 313.
- (44) Chierotti, M. R.; Rossin, A.; Gobetto, R.; Peruzzini, M. *Inorg. Chem.* **2013**, *52*, 12616.
- (45) Abraham, M. H. *Chem. Soc. Rev.* **1993**, *22*, 73.
- (46) Abraham, M. H. *J. Phys. Org. Chem.* **1993**, *6*, 660.
- (47) Cook, J. L.; Hunter, C. A.; Low, C. M. R.; Perez-Velasco, A.; Vinter, J. G. *Angew. Chem., Int. Ed.* **2007**, *46*, 3706.
- (48) Laurence, C.; Graton, J.; Berthelot, M.; Besseau, F.; Le Questel, J.-Y.; Lucon, M.; Ouvrard, C.; Planchat, A.; Renault, E. *J. Org. Chem.* **2010**, *75*, 4105.
- (49) Abraham, M. H.; Platts, J. A. *J. Org. Chem.* **2001**, *66*, 3484.
- (50) Abraham, M. H.; Grellier, P. L.; Prior, D. V.; Taft, R. W.; Morris, J. J.; Taylor, P. J.; Laurence, C.; Berthelot, M.; Doherty, R. M.; Kamlet, M. J.; Abboud, J.-L. M.; Sraidi, K.; Guiheneuf, G. *J. Am. Chem. Soc.* **1988**, *110*, 8534.
- (51) Laurence, C.; Brameld, K. A.; Graton, J.; Le Questel, J.-Y.; Renault, E. *J. Med. Chem.* **2009**, *52*, 4073.
- (52) Hunter, C. A. *Angew. Chem., Int. Ed.* **2004**, *43*, 5310.
- (53) Calero, C. S.; Farwer, J.; Gardiner, E. J.; Hunter, C. A.; Mackey, M.; Scuder, S.; Thompson, S.; Vinter, J. G. *Phys. Chem. Chem. Phys.* **2013**, *15*, 18262.
- (54) Arnett, E. M.; Joris, L.; Mitchell, E.; Murty, T. S. S. R.; Gorrie, T. M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1970**, *92*, 2365.
- (55) Beweries, T.; Brammer, L.; Jasim, N. A.; McGrady, J. E.; Perutz, R. N.; Whitwood, A. C. *J. Am. Chem. Soc.* **2011**, *133*, 14338.
- (56) Cronin, L.; Higgitt, C. L.; Karch, R.; Perutz, R. N. *Organometallics* **1997**, *16*, 4920.
- (57) The aryl fluorides and pyridyl lone pair have a low Lewis basicity relative to that of the nickel fluoride, as demonstrated by previous measurements and calculations of electrostatic potentials; see ref 55.
- (58) As previously established, the  $^{19}\text{F}$  resonance of the group 10 metal fluorides moves to high field on H-bonding or halogen bonding.<sup>36,55</sup> This behavior contrasts with that of group 4 metal fluorides.
- (59) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.
- (60) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.
- (61) Druce, P. M.; Kingston, B. M.; Lappert, M. F.; Spalding, T. R.; Srivastava, R. C. *J. Chem. Soc. A* **1969**, 2106.
- (62) Murphy, E. F.; Yu, P.; Dietrich, S.; Roesky, H. W.; Parisini, E.; Noltemeyer, M. *J. Chem. Soc., Dalton Trans.* **1996**, 1983.
- (63) Nikiforov, G. B.; Roesky, H. W.; Koley, D. *Coord. Chem. Rev.* **2014**, *16*, 258.
- (64) Herberich, G. E.; Barlage, W.; Linn, K. *J. Organomet. Chem.* **1991**, *414*, 193.
- (65) Murphy, E. F.; Murugavel, R.; Roesky, H. W. *Chem. Rev.* **1997**, *97*, 3425.
- (66) The high volatility of dichloromethane precludes its reliable use in our UV/vis titrations conducted with an automated plate reader with open wells.
- (67) (a) Zordan, F.; Brammer, L.; Sherwood, P. *J. Am. Chem. Soc.* **2005**, *127*, 5979. (b) Zordan, F.; Brammer, L. *Cryst. Growth Des.* **2006**, *6*, 1374. (c) Awwadi, F. F.; Willett, R. D.; Haddad, S. F.; Twamley, B. *Cryst. Growth Des.* **2006**, *6*, 1833.
- (68) Allen, F. H. *Acta Crystallogr., Sect. B: Struct. Sci.* **1986**, *B42*, 515.
- (69) Hydrogen bond distances estimated by placing hydrogens geometrically and refining positions using a riding model.
- (70) The association constant for  $\text{W}(\text{F})\{\kappa^3\text{-C}_6\text{H}_4\text{N}(\text{C}_6\text{H}_4)\text{C}(\text{H})\text{N}(\text{CH}_2)_2\text{NMe}_2\}(\text{CO})_3$  was conducted at 295 K, not 300 K, and therefore, the estimated  $\beta$  will be a slight overestimate relative to the other measurements.
- (71) Electronegativities from: Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry, Principles of Structure and Reactivity*, 4th ed.; Harper Collins: New York, 1993; Ti 1.54, Zr 1.33, Hf 1.3, Ni 1.91, Pd 2.2, Pt 2.28.
- (72) (a) Doherty, N. M.; Hoffman, N. W. *Chem. Rev.* **1991**, *91*, 553. (b) Grushin, V. V. *Chem. - Eur. J.* **2002**, *8*, 1006.
- (73) (a) Caulton, K. G. *New J. Chem.* **1994**, *18*, 25. (b) Mayer, J. M. *Comments Inorg. Chem.* **1988**, *8*, 125.
- (74) Reinhold, M.; McGrady, J. E.; Perutz, R. N. *J. Am. Chem. Soc.* **2004**, *126*, 5268.
- (75) Mezzetti, A.; Becker, C. *Helv. Chim. Acta* **2002**, *85*, 2686.
- (76) Holland, P. L.; Andersen, R. A.; Bergman, R. G. *Comments Inorg. Chem.* **1999**, *21*, 115.
- (77) Martínez-Prieto, L. M.; Melero, C.; Del Río, D.; Palma, P.; Cámpora, J.; Álvarez, E. *Organometallics* **2012**, *31*, 1425.



(78) Peruzzini et al. showed that the chemical shift anisotropy (CSA) of the  $^{19}\text{F}$  metal fluoride resonance of a Ni(pincer)F complex was higher than the CSA observed in other fluorine compounds (ref 32a). This may be related to ionic character.

(79) (a) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, 98, 1729. (b) Green, J. C. *Chem. Soc. Rev.* **1998**, 27, 263.

(80) X-ray structures. The F–M–F angles are as follows:  $\text{Cp}_2\text{TiF}_2$  96.0,  $\text{Cp}_2\text{ZrF}_2$  96.2,  $\text{Cp}^*_2\text{TiF}_2$  96.7,  $\text{Cp}^*_2\text{ZrF}_2$  99.6,  $\text{Cp}^*_2\text{HfF}_2$  98.5°. (a) Koleros, E.; Stamatatos, T. C.; Psycharis, V.; Raptopoulou, C. P.; Perlepes, S. P.; Klouras, N. *Bioinorg. Chem. Appl.* **2010**, 2010, 914580. (b) Bush, M. A.; Sim, G. A. *J. Chem. Soc. A* **1971**, 2225. (c) Nuss, H.; Jansen, M. Z. *Kristallogr. - New Cryst. Struct.* **2006**, 221, 206. (d) Kraft, B. M.; Lachicotte, R. J.; Jones, W. D. *J. Am. Chem. Soc.* **2001**, 123, 10973. (e) Rieth, R. D.; Brennessel, W. W.; Jones, W. D. *Eur. J. Inorg. Chem.* **2007**, 2007, 2839.

(81) Ammann, C.; Meier, P.; Merbach, A. E. *J. Magn. Reson.* **1982**, 46, 319.

(82) Nova, A.; Erhardt, S.; Jasim, N. A.; Perutz, R. N.; Macgregor, S. A.; McGrady, J. E.; Whitwood, A. C. *J. Am. Chem. Soc.* **2008**, 130, 15499.

(83) Gassman, P. G.; Campbell, W. H.; Macomber, D. W. *Organometallics* **1984**, 3, 385.

(84) Druce, P. M.; Kingston, B. M.; Lappert, M. F.; Spalding, T. R.; Srivastava, R. C. *J. Chem. Soc. A* **1969**, 2106.

(85) Murphy, E. F.; Yu, P.; Dietrich, S.; Roesky, H. W.; Parisini, E.; Noltemeyer, M. *J. Chem. Soc., Dalton Trans.* **1996**, 1983.

(86) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Crystallogr.* **2009**, 42, 339.